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Applications of Supersonic Waves.

SUPERSONIC waves have recently been made use of to examine their physical, chemical, and metallurgical applications[1] which are numerous. They have been used for destroying labile equilibria, starting chemical reactions and for studying their electrochemical and photo-chemical effects. Supersonic waves have also been studied in relation to their effects on very small particles such as effects of a colloidal-chemical nature, the production of disperse systems, the aggregation and flake formation of smoke, dust, and fog particles. As far as the materials of construction are concerned, the waves have been applied to improve metallic constructional materials and also to the testing of materials. Much of this can no doubt be regarded as new as far as metallurgical applications are concerned.

Supersonic waves are waves with frequencies lying above those in the range of audible sound. These high-frequency waves can be transmitted in any required direction, and, further, great energy intensities can be obtained. The dispersion of the waves depends on the conditions within the medium through which they are being transmitted.

The most important method of producing supersonic waves is that of converting electrical vibrations into mechanical vibrations. In this method, frequencies up to about 50 kHz are produced by a magneto-striction sound producer. What actually happens is that the waves are produced by the mechanical distortion of a ferro-magnetic body situated in a magnetic field—the so-called magneto-striction—but for higher frequencies a piezo-electrical sound producer is used exclusively. In this way, frequencies up to 200 million Hz can be reached. By piezo-electrical phenomena is meant the well-known mechanical distortion of certain crystals when placed in an electric field which may be traced to movement of the ions. This distortion only occurs if the electric field has a component in the direction of what are known as electrical axes of the crystals Mechanical vibrations are set up in the crystal of the same frequency as the applied alternating field. Mechanical devices employing supersonic waves were in use in the Great War for locating the presence of submarines.

In order to understand all the effects resulting from supersonic waves, it is necessary to have a knowledge of the physical properties and effects of intense waves. The influence of these waves always implies mechanical loading, and therefore phenomena are to be expected which arise from mechanical shocks. Where pressures are exceptionally low, supersonic waves may be used for degassing liquids, and there are other numerous possibilities of a physical nature. The effect of bombardment with intense supersonic waves can be seen, in its destructive aspect, by the roughening produced on the edge of a steel knife—after a bombardment lasting ten minutes. The actual damage is in this case produced by "cavitation" effects resulting from the waves.

So far only the mechanical effects of supersonic waves have been referred to, yet their thermal effects require consideration. The periodic thermal effects produced by adiabatic temperature changes are so very small even in the case of the strongest supersonic wave producers that negligible results may be expected. On the other hand, the non-periodic temperature changes resulting from the absorption of supersonic energy can reach considerable magnitudes and must be taken into consideration when they are not compensated for by cooling. Specially strong heating occurs at boundary surfaces, and pieces of cork may be burnt when coming into contact with a supersonic wave emitter. Also, consequences of an electrical nature may be expected with the largest sound strengths.

The vibrations set up in bodies by supersonic waves have already been referred to, and phenomena resembling mechanical "shaking" would therefore be expected to destroy labile conditions of equilibrium. The consequences of the like require, therefore, no further explanation, and the following instances may be cited:—The avoidance of superheating at boiling or melting points, the crystallisation of supersaturated solutions, and the explosion of substances particularly susceptible to the touch.

Chemical reactions which arise as a result of wave treatment may be divided into two groups from the point of view of the probable mechanism concerned. First, reactions which occur as a result of activation of dissolved gases following cavitation effects, and secondly, the breaking down of highly polymerised substances. Various oxidations, as well as the formation of very small quantities of acids containing nitrogen, and of ammonia, are the best known of the first group. It could be shown that these reactions would not occur in the absence of dissolved gases in the liquids. They are dependent on the formation and breakdown of cavities. The amount of the substances produced, resulting from exposure to the waves, is very small. Such substances as gelatin, gum-arabic, and cane sugar, &c., can be separated into molecules of simpler structure. Again, it has been found in some cases that speeds of chemical reaction can be increased by the action of supersonic waves. In some cases the increase results for the activation of dissolved gases; in others thermal effects may be chiefly responsible.

The first systematic experiments on the electrochemical effects of supersonic waves were made by Schmid and Ehret,[2] who observed that the waves affected the passivity of metal. They found that supersonic waves affected the passivity as a result of mechanically breaking up the protective covering

layer, for example, in the case of iron in concentrated sulphuric acid, as well as affecting the chemical passivity, for example, in the case of iron in concentrated nitric acid. The passivity of the iron could in both cases be hindered or decreased as a result of such wave treatment. The effect of the waves consists obviously in the breaking loose of the mechanically superimposed covering layer promoting passivity. The changes involved in the action on the chemical passivity are not explained.

There are possibilities in the laboratory of precipitating aluminium and magnesium electrolytically out of aqueous solution by means of supersonic waves, and again of nickel-plating. In most cases depolarisation occurred on exposure to these waves, in exceptional circumstances polarisation. The method has shown quite remarkable results regarding the electrolytic separation-potential of hydrogen. Young and Kersten report that when iron is deposited electrolytically on a copper cathode a deposit in the form of fine parallel ridges is produced by the action of supersonic waves, the distance between the ridges corresponding to half their wave length. A similar form of ridge formation is produced on developing a photographic plate, after exposure to the waves, which illustrates the chemical action induced. Luminescence in liquids is also produced.

Attempts to disperse metals by means of supersonic waves often lead only to very coarsely dispersed systems. According to Claus, highly dispersed systems are obtained when metals during electrolysis or chemical reaction are exposed to supersonic waves. On the contrary, other investigations have shown that non-metallic particles such as smoke, dust, and fog, may tend to collect together or form flakes. This occurs to a very considerable extent judging by the rate at which the particles settle under gravity and by their appearance.

Claims have been made that the physical properties of steel, especially the strength, have been improved by high-frequency vibration, as well as a considerable reduction in the time required for nitriding and in depth of penetration of the nitrogen. There are indeed, numerous metallurgical processes which proceed at considerably greater speeds, or proceed at the same or even at higher speed with lower temperature, as a result, it is stated.

Sokoloff[3] has shown that molten zinc, when allowed to solidify under the action of supersonic waves of high frequency (650 to 4500 kHz) showed a different crystal structure compared with other melts when solidified without the wave treatment. The crystal structure, as a result of the wave treatment, was of finer grain, and, it should be remarked, of more needle-like structure. It has further been suggested that melts could be degassed by the use of these waves. It is unnecessary to make a too sharp distinction between ordinary sound waves and supersonic waves as far as their effects are concerned, since many effects found with supersonic waves could afterwards be produced by the use of sufficiently intense sound waves.

The apparatus used by Schmid and Ehret in their experiments on the effect of supersonic waves on molten metals during solidification has been fully described by them. Their apparatus has only been developed as far as necessary for small-scale laboratory experiments.

The accompanying illustration due to Schmid and Ehret shows the effect of audible sound waves on pure metal and alloys. A marked increase in grain refinement has taken place.

These results suggest that the formation of coarse dendritic structures is resisted by sound waves; for example, in the case of silumin one can observe clearly a breaking up of the needle-like structure. The increase in the fineness of grain corresponds also to an alteration of the mechanical properties. For example, the Brinell hardness is 52 ± 1 kilos. per square millimetre for antimony exposed to the sound waves, and is 34 ± 1 kilos. per square millimetre for antimony unexposed, whilst the corresponding values for duralumin are 96 ± 4 kilos. per square millimetre, and when unexposed 78 ± 7 kilos. per square millimetre. In the case of silumin an alteration in Brinell hardness could not be determined with certainty.

Masing and Ritzau[4] have experimented with sound

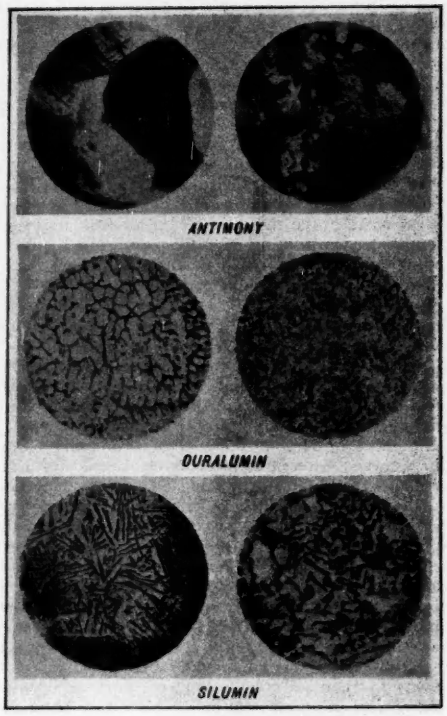

Photo-micrographs of Melts Solidified under the Action of Sound Waves (right side of illustration) and Identically Similar Metals not Subjected to Sound Waves (left side).

waves of yet lower frequency (500 Hz). In particular, they attempted to produce a fine dispersion of lead in aluminium to make this material more easily machinable in automatic machines. Schmid and Ehret carried out similar experiments and by using a stronger wave emitter were able to produce a considerably better result. Lead added to molten duralumin as lead chloride which was reduced by the aluminium resulted in large lead inclusions. The effect of treating this material with sound waves of 500 Hz and 10 kHz was to disperse the lead so as to form much smaller and numerous lead inclusions. This left no doubt whatever that a grain refining

action takes place and that the distribution of one metal in another can be altered.

No further results of the effect of supersonic waves are, it is stated, available regarding other metallurgical processes, but it is perfectly clear that the possibilities of sound-wave treatment have not been exhausted, and even the simplest mechanical devices for producing ordinary vibrations may perhaps yield important practical results.

Another application of the waves is in testing materials. Tubes or rod of ferro-magnetic material may be torn asunder by subjecting them to the magneto-striction effect with large amplitudes of vibration. Newton Gaines[5] has pointed out that determination of the tensile strength of material for alternating load can be carried out in very short time by means of high-frequency vibrations. With sound frequencies of 10 kHz, it is possible already to reach thirty-six million load reversals in one hour. Further investigation is necessary to find if the high-frequency alternating strength is similar to the alternating strength under low-frequency load reversals, or whether at least a simple relationship exists between the two strengths. According to preliminary determinations of Gaines, the strength values obtained by both methods appear to agree in order of magnitude with one another.

Iron and steel specimens allow supersonic waves to pass through them very easily. It is possible to pass the waves without difficulty through a depth of many metres of steel provided the metal is free from defects. However, if discontinuities occur in the steel, such as cracks or blow-holes, then the passage through of the waves is greatly restricted and only a small proportion is transmitted whilst back reflection of the waves and also absorption under certain circumstances is very great. Since these waves spread out or disperse in a material like rays issuing from a source, it is possible to discover the presence of defective places in a material by supersonic wave "shadows," if the direction of the waves travelling backwards is known. This method of locating failures in a material is at present in an early stage of development, and requires further study in view of its practical possibilities.

The operation of agitating moulds for the purpose of producing grain refinement during solidification of molten metal has been the subject of investigation already and is well known.

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[2] *Z. Elektrochem.*, 1937, 43, 408–415.
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[4] *Z. Metallkunde*, 1936, 28, 293–296.
[5] *Physics*, 1932, 3, 209.

The Dusseldorf Rail Congress.

By HUGH O'NEILL.

Permanent-way engineers are still seeking the perfect rail. Presumably they will not be satisfied until provided with an article at a reasonable cost which, whilst neither wearing in service, cracking under heavy dynamic loading nor corroding in tunnels, will yet possess enough ductility to be bent into curves and crossings. In the absence of special research tracks rail merit has to be assessed on actual running experience, and writers in the past have complained of the paucity of available information as to the service performed by different types of rails. In 1935, for instance, it was recorded that any real progress seemed unlikely "until greater publicity is given to the results obtained by the various bodies concerned." This situation would now appear to have been remedied, for amongst the thirty-four papers presented at the Fourth International Rail Assembly held at Düsseldorf last September, at least five provided first-hand information regarding service performance. One of these was by an English engineer and happened to be the only contribution from Great Britain, so with this exception, the following *résumé* of the papers refers always to flat-bottom rails.

Since all but two of the contributions to this triennial Congress were presented by Continental writers, the amount of attention given to specially hard track materials is not surprising. Such are the Klöckner compound rail, which is rolled from a duplex ingot so as to have a hard wearing head (Brinell No. 320) differing in composition from the web and base (Brinell No. 150); and the Maximilianshütte rail, whose top table is quenched from 800 deg. to 200 deg. Cent. in about one minute, and consequently becomes martensitic. These articles are strangers to us, chiefly because it is doubtful whether they will pass the standard falling weight test. It may be recalled that the disaster at St. Neots in 1895 was ascribed to the presence of a brittle martensitic structure in the surface of a rail, and one might speculate as to the effect of this failure upon British engineers. On the other hand, rails which by means of controlled spray quenching have a sorbitic head are universally appreciated.

Considering first the results of service behaviour, a paper by Hervig gave an account of the system of reporting rail fractures adopted by the German State Railways. In the twelve months prior to May, 1938, 360 breaks of ordinary rails were reported, and the distribution of these between the different parts of a rail have been analysed. During that year 32 per cent. of the fractures occurred in the head and 51 per cent. in the web, so that the prevalence of web failures might be considered in relation to a paper by Baud proposing a new design of rail web, which is thicker than usual at the top, and thinner where it joins the foot. Daussy called attention to the weakness of flat footed rails at the centre of the bottom flange, where the chilled skin and columnar zone of the ingot take up positions which give an unfavourable macro-structure. By means of a new series of rolling passes the chilled skin is broken up and the columnar crystals are bent parallel to the rail surface.

As regards harder rails, Hervig's evidence was to the effect that casualties were relatively high on their introduction, but behaviour subsequently improved, whilst incidentally basic Bessemer steel appears to be as good as open-hearth steel. Mandel gave an analysis of twenty-five years' statistics of curved track obtained on the Hamburg Elevated Railway. Bessemer rails with a tensile strength of 38–45 tons per square inch provided better wear resistance than ordinary open-hearth rails with a tensile strength of 48–54 tons, but chemical analyses are not given. Compound steel rails are now used on the curves, and it is found that their life is approximately four times that of ordinary open-hearth rails, whilst corrugations are less developed and more easily removed when the special grinding car is sent out to deal with them. The cost of compound rails is, of course, very high, and the economics of their use must be considered in relation to scrap values. Kuhn pointed out in con-

nection with tram tracks that the compound rail is too expensive for ordinary straight lengths, and incidentally plain rails of 45–48 tons tensile gave fewer breaks than those of over 50 tons tensile.

The results of ten years' observations in heavy traffic of rails having a tensile strength of 58–62 tons per square inch were discussed by R. Walzel. The electric furnace steel under investigation contained 0·6 per cent. carbon, 1·8 per cent. manganese, with sulphur and phosphorus at about 0·02 per cent. each. The amount of wear on the outer rails of curves was only about one-third that of ordinary steel having a tensile strength of 44–48 tons per square inch, and there appeared to be less deterioration at the joints due to end batter. The corrosion of steels of this composition and containing 0·25 per cent. copper has been examined by accelerated laboratory tests, but service results are not yet available. By heat treating the material to an ultimate strength of 85 tons per square inch, crossings can be made which gave from one-fifth to one-tenth the rate of loss of height by impact crushing, as compared with ordinary cast steel crossings.

A paper by C. J. Allen, of the L.N.E.R., discussed the changes in composition and properties of British rails since 1880, and gave unqualified support to the use of the higher manganese (1·1 per cent.), lower carbon (0·55 per cent.), type of material. For a given tensile strength it is shown that the medium manganese rail gives good ductility values, which the author associates with greater toughness in service. The results of prolonged track experiments are given, but without details, and the importance of work-hardening capacity is mentioned, together with the possibility of pre-service cold-working treatment. Controlled cooling through 550 deg. to 300 deg. Cent. after rolling, in order to reduce stresses and shatter cracking, is recommended, and the paper concluded with a detailed account of the Sandberg sorbitising process. Only laboratory test values are given, the chief point being the rise of yield ratio from 60 to 85 per cent. by the treatment. It is stated that L.N.E.R. service wear tests have decided a policy of laying sorbitised rails in electric train tracks and those where rail life is shorter than ten years. It is emphasised that such rails offer no additional resistance to severe corrosion, and after lengthy experiments in tunnels in which both copper bearing and chromium steel rails have been tried, it has been decided that painting is the most promising method of prolonging rail life. This incidentally was a treatment introduced by MacDonald as far back as 1899. Friedli gave details of heavy corrosion losses in steam-operated tunnels, heat-treated rails being very slightly inferior to soft rails, but somewhat better than untreated low alloy rails of about 330 Brinell.

Passing from service tests to those which may be carried out in the laboratory, R. Kühnel discussed the methods now applied and summarised the existing requirements of thirty-four different countries. He contends that tensile strength and toughness, as indicated by tensile and bend tests, suffice to show the degree of resistance to fracture and to wear, and he would give the manufacturer wide latitude regarding chemical analysis. It is interesting to note that Hungarian specifications permit a maximum sulphur content of 0·08 per cent., whilst five countries tolerate 0·1 per cent. of phosphorus. The testing of ordinary, compound, and heat-treated rails was detailed by Ros and Bianchi, the wear properties in particular being considered on the basis of Amsler machine results, together with track tests on the St. Gothard line. Amsler tests on natural hardness rails (170–300 Brinell) and heat-treated rails (200–400 Brinell) showed reduced wear with increasing Brinell number, the two types following two separate relation curves. Track wear was computed on a basis of reduction in section per 10 million gross tons of traffic, and confirmed the general inference obtained from the laboratory tests. The authors consider that manufacturers are now able to satisfy all local track requirements, and fix an upper limit of hardness for the rail at 420 Brinell, beyond which there is a danger of breakage.

Cracks in rails are generally produced by alternating fatigue stresses or by sudden shocks. Bartel found no relationship between service life and notched bar impact strength, whereas Forcella reported that for equal tensile strengths the steel with the greatest notched bar value had the greatest alternating bend strength, and gave the best results in the drop test. Schulz examined the proper application of various laboratory tests, whilst Siebel emphasised the necessity for specialised wear machines, and Zocchi discussed wear in terms of thermal, recrystallisation and strain-hardening effects. Eichinger's experience showed that it was necessary to make wear test conditions more stringent than those in service. He reported Amsler machine results on ordinary, heat-treated and compound rail steels with pure sliding friction and under wet and dry conditions. He also considered the exfoliation of tyres, but this received more attention in a paper by C. Benedicks,* who commented upon previous Amsler results in which the presence of water caused bigger wear and more pronounced exfoliation. Benedicks introduced the consideration of season cracking effects and observed that a diamond will rupture wet glass at half the stress required for dry glass. Transverse cracks on the tread, such as might be caused by braking, will cause plastic flow and intermittent exfoliation of the adjoining material under the action of rail pressure. Non-metallic inclusions should be kept at a minimum to hinder the breaking off of the deformed patches, whilst the columnar crystalline zone of the blanks should either be removed or deformed during tyre manufacture so as to prevent the dendrites running out vertically to the tyre surface. Attempts to cure tyre exfoliation on the German and Swedish railways have taken the form of increasing the tensile strength, but the trouble has by no means been completely eliminated. Rail corrugations constitute another problem with which R. Kühnel dealt in detail, the suggestion being made that the hard bright patches are associated with vibrations in the rolling mill and the surges of vehicles induced by braking. Pressure figures developed between rail and tyre during braking had similar shapes and orientations to corrugation patches, and Amsler test rollers also develop rectangular corrugations.

As an alternative to the use of standard comparison pictures, Teodorescu and Nadasan described a quantitative method of measuring sulphur segregation in rails. A transparency is made from the ordinary sulphur print and traversed with a photo-electric cell. Incidentally the present writer takes sulphur prints directly on to transparent Kentmere film paper, from which numerous positives can be printed. The use of such film paper would presumably avoid the making of the above transparency, but it seems doubtful whether this degree of quantitative examination is justified in any case.

* *Stahl und Eisen*, 1938, 58, page 999.

Internal stresses in individual rails may be examined by the change of dimension method, as reported in Ros and Bianchi's paper, but Schönrock also gave particulars of an X-ray back reflection technique taking spectrograms in one vertical and two oblique directions. His results account for the fact that cracks in rail heads caused by internal stresses are nearly always found to be in the direction of rolling. Brandenberger reported the average crystal sizes and the amount of lattice disturbance from X-ray spectrograms of normal, heat treated, and compound steels, and of Eichinger's wear test specimens. Three papers dealt with thermal stresses in the track from the point of view of warping, and that by Hüttner included results obtained by photo-elastic methods. Warping stresses are of interest in connection with the production of jointless track, and six papers studied the arc, thermit, and resistance methods of welding, test results being provided together with a discussion of testing methods. Taken as a whole, the contributions to this assembly provide an imposing review of the present position of European rail technology.

Ageing.

By MARIE L. V. GAYLER, D.Sc. (Mrs. HAUGHTON), National Physical Laboratory.

(*Continued from October issue.*)

III. FACTORS AFFECTING AGE HARDENING.

(a) *Quenching Temperature.*—The temperature of quenching has a very marked effect on the subsequent ageing of the alloy. The solution treatment should be carried out at a temperature not lower than the minimum temperature for maximum solid solubility of the phase or phases responsible for age hardening. In practice, however, it is generally more satisfactory to quench from a temperature somewhat above that necessary for complete solution. In certain cases it is essential to quench from temperatures considerably above the solid solubility limit,[37] in order to develop room temperature ageing at all, although quenching from just above the line should preserve the solid solution intact. Two explanations for this fact have been put forward—(*a*) that the higher temperature serves better to suppress the transformation and consequently permits the development of the ageing process,[38] and (*b*) that the higher quenching temperature results in a greater strain effect and hence facilitates the subsequent ageing process.[35] The mechanical properties generally improve as the quenching temperature is raised.

(b) *Temperature of Heat Treatment.*—The temperature at which the quenched alloy is aged has a very profound effect on its physical and mechanical properties. If quenched duralumin be stored in iced water at 0 deg. Cent.,[39] the ageing process is retarded very considerably; while at the temperature of liquid air this alloy appears to remain permanently soft.[40]

The temperatures of heat treatment which cause the ageing process to be completely inhibited, or else very much retarded, are peculiar to each alloy system. For example, the effect of a heat treatment at, say, 250 deg. Cent., on duralumin is very different from that observed in the case of Be-Cu alloys. The former attains maximum hardness within the first hour of heat treatment and then immediately softens rapidly, while the latter hardens and remains at a constant figure for at least 107 days. Furthermore, alloys of different compositions, but belonging to the same system, also differ in their response to heat treatment. An alloy containing 2·5 per cent. Be attains a different maximum hardness in a shorter time than another containing 1·5 per cent. Be heat treated at the same temperature.

(c) *Chemical Composition.*—Change in chemical composition is a most important factor for the following reasons:—

(i) It may influence the rate at which age hardening will take place.

(ii) It may decrease or increase the maximum age hardening which can be attained.

The influence of altered composition depends on whether the added constituent simply reduces or increases the solid solubility of the phase which precipitates during age hardening, or whether it alters the solid solubility of the phase by the formation of a new phase which may or may not go into solid solution. Generally speaking, such a phase is usually insoluble, and hence the amount of the phase responsible for age hardening is reduced; on the other hand, an increase in age hardening may result if the new phase goes into solid solution.

For example, the effect of excess magnesium on the ageing of an aluminium alloy containing 1·6 per cent. Mg_2Si causes a reduction in the solid solubility of Mg_2Si, which, in its turn decreases the age hardness possible and the rate of ageing,[3]

The effect of small additions of other elements on the ageing of 4 per cent. Cu-Al (0·3 per cent. Fe; 0·3 per cent. Fe, and 0·24 per cent. Si; 0·24 per cent. Si; 0·5 per cent. Mg), is very marked. The addition of 0·3 per cent. Fe inhibits the ageing at room temperature and forms an insoluble complex phase; 0·24 per cent. Si has no effect; 0·5 per cent. Mg increases the age hardening.[14]

The addition of 0·12 to 0·15 per cent. Fe to 2 per cent. Be-Cu[41], causes the appearance of a new phase, and such alloys show an increased mechanical strength, both in the quenched and in the age-hardened states, combined with greater ductility and resistance to softening after prolonged heating at 300 deg. Cent., as compared with the Fe-free alloy, which loses hardness after 10–14 hours at this temperature. The amount of beryllium in solid solution for a given content is, however, reduced. The addition of aluminium to the beryllium-copper alloys also decreases the solid solubility of beryllium in copper not by the formation of a new phase, but by simply reducing the limits of the solid solubility of the β phase; consequently the hardening obtainable with beryllium in these alloys is decreased and ageing takes place with a lower beryllium content.

Small amounts of added constituents may therefore have a profound effect on the age hardening of alloys.

(d) *Grain Size.*—The influence of added constituents now leads to a consideration of the effect of grain size on hardening. The results of various investigators on the effect of grain size on ageing have been somewhat conflicting. It was first concluded that grain size had a marked effect—apart from the fact that the solution process prior to quenching is a function of grain size.[42], [43], [44], [45] Later, however, it has been shown that there is no qualitative difference in the precipitation process in single and poly-crystalline material,[46] but that the differences previously observed were due mainly to differences in the rates of diffusion.

(e) *Cold Work, Including Lattice Distortion.*—Change in chemical composition has a marked effect on the process of age hardening, and the process

of diffusion is intimately connected with the latter. Furthermore, cold work entails lattice distortion; it is essential, therefore, to find out to what extent the latter has an effect on diffusion.

Mooradian and Norton[47] have carried out an X-ray investigation on the diffusion of two metals into each other. They deposited alternate thin layers of Cu and Au, Au and Ag, Cu and Ni, and Ni and Co by electrolysis and examined the structures by X-ray analysis before and after heat treatment for 24 hours at specific temperatures. Their results show that lattice distortion in the original samples is not an aid to diffusion since it disappears completely before diffusion starts. These authors consider that lattice distortion may even be a distinct hindrance and its removal a necessary factor, before easy diffusion can take place. These conclusions differ from those generally accepted, viz., that distortion accelerates diffusion. Mehl and Barrett,[47] discussing Mooradian and Norton's results, remark: "The few measurements available show that diffusion along grain boundaries is much more rapid than within crystals, and since slip planes are in many ways similar to grain boundaries, we may expect a similar effect to be present in deformed metals. Apart from this argument, various experiments are available which show the effect of distortion on accelerating diffusion."

It is obvious that more research is needed to explain these differences.

Fraenkel,[48] amongst others, has studied by means of hardness and electrical resistivity measurements the effect of cold work on duralumin. He found that (*a*) the rate and amount of hardening at room temperature increases with the degree of cold work given to the alloy; (*b*) there is a corresponding increase in the electrical resistivity in comparison with that observed when the alloy ages normally; and (*c*) an increase in the rate at which this change takes place.

These results show that cold work accelerates age hardening. It might therefore be deduced that this is indirect evidence for an acceleration in the rate of diffusion. Reference should, however, be made again to Mooradian and Norton's conclusion that lattice distortion disappears completely before diffusion takes place and that in their opinion it is not an aid to diffusion and may even be a distinct hindrance. This view, however, does not include the possibility of the existence of breakdown structures.

(f) *Quenching Stresses.*—The existence of quenching stresses has been determined by three methods: (1) measurement of dimensional changes on machining a quenched alloy; (2) measurement of lattice parameter; (3) microscopic evidence.

(1) Portevin[49] carried out measurements to see whether strains were set up in a specimen as a result of quenching. He rapidly cooled cylindrical specimens of copper, nickel, and steel by quenching in water, and found that internal stresses were set up which put the surface in tension and the central region in compression. He made further tests with steels and alloy steels and found that the more severe the cooling the greater the internal stresses set up. Later, Grogan and Clayton[50] carried out similar experiments with four aluminium alloys and measured the dimensional changes occurring on machining the alloys after heat treatment. Their results also showed that stresses are set up as the result of quenching and that they are greatest in the specimen which has been most severely quenched.

That such quenching stresses exist is of great importance, since they bear a definite relation to the subsequent age hardening of the alloys.

(2) Stenzel and Weerts[17] found that the lattice parameter of a 5 per cent. Cu-Al alloy quenched from 530 deg. Cent. and aged at 150 deg. and 225 deg. Cent. until complete precipitation of $CuAl_2$ had taken place was definitely larger than that of pure aluminium. They attributed this anomaly to the effect of strain induced by precipitation of $CuAl_2$, which conclusion was later proved unlikely by Phillips and Brick.[35]

Phillips and Brick carried out an extensive investigation on the effect of quenching strains on the lattice parameter and hardness values of the high purity of 5·4 per cent. Cu-Al alloy. Their results corroborated those of Stenzel and Weerts, but they found that the abnormally large lattice parameters markedly increased as the size of the specimen increased. They considered that it seemed probable that anomalies appearing in the course of precipitation were related to, or rather originated in, the 550 deg. Cent. solution treatment and the subsequent quench. They therefore carried out further experiments which showed that large specimens (½in. diameter) cooled in still air or in boiling water, had lattice parameters identical with those of wires 0·07in. diameter, heat treated similarly. Furthermore, the X-ray photograms of these specimens had reflection lines somewhat sharper than those of the more drastically quenched alloys. Phillips and Brick considered that these data indicated that strain—originating in the quenching—was responsible for the previously observed large parameter values. These investigators correlated their results with hardness measurement and found that the rate and magnitude of the age-hardening process was greatly influenced by the previous quenching speed, and that although, perhaps, it was impossible to cool a supersaturated solid solution to room temperature rapidly enough to suppress the breakdown of the metastable phase without introducing strain, a ½in. rod cooled in still air seemed to approach this ideal most closely. No precipitation occurred during the cooling process, as shown by the parameter value, and up to the end of 30 days practically no hardening was observed. In the same period marked increases in hardness were found in the other specimens, reaching a maximum in the rod cooled in $CaCl_2$—water mixture at −20 deg. Cent. The corresponding parameter values range from no change in the air-cooled rod to a small decrease in the more severely quenched specimens. Phillips and Brick hold the view that the decrease did not seem, at first thought, to be connected with a precipitation process that normally would involve an increase in the parameter value. Nor do they consider that it could be due to a re-solution of compound precipitated in some way by quenching stresses, since this would involve an increase in the metastability or free energy of the lattice and probably a softening effect. These authors think that it seemed likely that the age hardening at room temperature was related in an unknown manner to a partial relief of the original quenching strain, for although the parameter of the quenched specimen had decreased slightly, it was still considerably above that of the non-ageing, air-cooled specimen, and it seemed possible that the relief of strain had been accompanied by an actual precipitation. They remark: "With one exception, the lower the lattice parameter value of the quenched alloy, the less the magnitude of room temperature age hardening. Although our data suggest the possibility of an actual precipitation, the evidence is admittedly too meagre definitely to establish this point."

(3) Quite recently Fink and Smith[51] have shown by microscopic analysis the presence of quenching strains in a 5 per cent. high-purity copper-aluminium alloy. They polished a specimen before quenching, and on examining it under the microscope after quenching without repolishing found that grain boundaries and slip planes were clearly revealed by the relief produced by plastic deformation, *i.e.*, by quenching stresses. (The change in direction of the slip bands across the grain boundaries distinguished them from scratches.) Fink and Smith also found that if the specimen was heat treated for 2 hours at 200 deg. Cent. and then etched with Keller's reagent, markings were developed which were identical with those previously associated with precipitation. These authors consider that the structure shows the coincidence of the loci of the precipitate and the slip bands and grain boundaries. Fink and Smith also quenched polished specimens in boiling water and in oil at 153 deg. Cent. (thus reducing the quenching stresses), and found no evidence of slip, which is further confirmation of Phillips' and Brick's[35] results. The character of the precipitate which appeared after subsequent ageing for 2 hours at 200 deg. Cent. showed that general precipitation had taken place without any tendency to concentrate on slip planes. The authors consider that the precipitate is probably of a Widmanstätten nature.

(g) *Hydrostatic Pressure.*—The effect of hydrostatic pressure on the ageing process has also been investigated. Tammann and Hartmann[52] carried out some experiments on duralumin. They found little, if any, change in the rate of age hardening when the specimen was tested under a pressure of 1500 kilos. per square centimetre, but when this pressure was doubled the ageing was retarded appreciably.

IV. THEORY OF AGE HARDENING.

The characteristics accompanying the process of age hardening and factors which alter its magnitude and rate have been briefly surveyed; the question arises, is there any theory which can correlate these facts?

Merica, Waltenberg and Scott[53] put forward in 1919 the theory of "dispersion hardening" to explain the phenomenon of age hardening in duralumin. Later, the results of many investigators, to which reference has been made, raised some doubt as to whether this simple theory adequately explained all the available data.

Briefly, the original duralumin theory stated that:—

(*a*) Age hardening depends on the solubility-temperature relation of the hardening constituent.

(*b*) This constituent is $CuAl_2$.

(*c*) Hardening is caused by the precipitation of $CuAl_2$ in some form other than atomic dispersion, and probably in a fine disperse in molecular, colloidal or crystalline form.

(*d*) The hardening effect was considered to be related to particle size; critical dispersion giving maximum hardness.

Hardening, according to this theory, is due to the increasing hardening effectiveness of particles of size greater than atoms, whereas softening is due to the decrease in number of these particles as their size increases.

Fraenkel and Seng[54] were the first to raise objection to this theory, calling attention to the fact that during ageing at room temperature, duralumin showed an increase in electrical resistivity which is not in accordance with the electrical properties of solid solutions. He suggested that there was the possibility that the mechanism of age hardening at room temperature might be essentially different from that at higher ones (150 deg. to 250 deg. Cent.). Various modifications of the theory regarding the process by which precipitation hardening may take place have been put forward by Jeffries and Archer, Honda, Gayler, Preston, and others, but no direct proof of the precipitation of $CuAl_2$ in Cu-Al. alloys aged at temperatures up to 300 deg. Cent. has been forthcoming. Schmid and Wassermann[33] identified by X-rays the existence of $CuAl_2$ in annealed duralumin, but not during age hardening, while Wassermann and Weerts during ageing at high temperatures identified a phasewhose structure is intermediate between that of $CuAl_2$ and the Al solid solution.

Wassermann[55] also found the first indications of $CuAl_2$ at 200 deg. Cent. after 70 days at that temperature, and that $CuAl_2$ increased in amount with time at the expense of the intermediate phase. Also Preston,[25] Calvet, Jacquet and Guinier,[26] have recently shown that $CuAl_2$ is not precipitated during ageing at room temperature.

These facts cannot be explained entirely by the simple precipitation theory.

Previous to the publication of the X-ray results just mentioned, Cohen[18] and Gayler[10] put forward theories of age hardening which were very similar. They showed that two maxima occur on time-hardness curves during ageing, and both investigators deduced that ageing takes place in two stages. The first is considered as the pre-precipitation stage and the second as that due to precipitation proper. Cohen considered the first stage is due to "knot" formation, and Gayler that it is associated with the diffusion of atoms to planes about which precipitation proper will ultimately take place. She considered, too, that the second stage of ageing took place concurrently with the former, and that both processes took place within a wide temperature range, the rate of each process depending upon the temperature of ageing and proceeding to a maximum. The first stage tends to be or is gradually replaced by the second.

The recent X-ray analysis of single crystals of Cu-Al alloys already referred to confirms the fact that the first stage of the ageing process is due to the diffusion of solute atoms to planes about which precipitation proper will ultimately take place. The exact mechanism of the precipitation of discrete particles has, however, still to be solved.

Fink and Smith,[51] however, have suggested that the first ageing peak is due to plastic deformation during quenching, and have put forward the micrographical evidence, to which reference has been made, of quenching strains in copper-aluminium alloys. They consider that certain regions of the quenched specimen would suffer plastic deformation which would accelerate the rate of precipitation in them, while age hardening would occur—presumably normally—in other parts which had not suffered plastic deformation. The resultant of the two processes would give double ageing peaks on the hardness-time curves. The authors consider that the simple precipitation theory is sufficient to account for all known data of age hardening. The most recent X-ray data have, however, shown conclusively that $CuAl_2$ is not precipitated at room temperature, which fact is

essential if the simple precipitation hypothesis holds.

V. PRACTICAL APPLICATIONS.

The importance of age hardening to industry is far-reaching. There is scarcely need to refer to the enormous uses of heat-treatable aluminium alloys, which are daily increasing in quantity and variety. In aircraft construction duralumin still holds supreme, but other alloys are being developed which, in the "as cast and heat-treated" state, possess properties superior to duralumin when exposed to temperatures above room temperature for considerable periods.

The production of new alloys, the development of their solution treatment and subsequent ageing heat-treatments, so that the most suitable material may be made available for a specific purpose, is a subject of vital importance to industry.

Practical application has been made of the use of the possible retardation of ageing; for instance, light alloy rivets are now shipped abroad stored in ice boxes, so that they may arrive ready for use in the soft "as-quenched" state.

On the other hand, accelerated precipitation hardening has become a commercial proposition. In America[56] this process has been termed "double ageing," and consists of heating the alloy to the solution temperature, quenching, and reheating to a suitable precipitation temperature, strain hardening, and again reheating to a suitable temperature. The strain hardening may be induced either by the rate of cooling from the first reheat or by cold working.

It has been seen that "growth" may take place to a very appreciable extent in ferrous and non-ferrous alloys if they are machined immediately after drastic quenching; also that this is reduced if the chilling is less severe and that it is not detectable if machining is carried out after the normal age-hardening process is complete. These facts are of immediate importance when materials of definite dimensions are required.

Growth of another type occurs when a cast alloy undergoes decomposition due to the suppression of a transformation. This, too, is an ageing problem, for die castings of Al-Zn alloys (80 per cent. Zn) shrink during the ageing of the alloy at room temperature owing to the decomposition of the Al phase. Fuller and Wilcox[57] have found that the addition of magnesium and copper greatly retard this decomposition and if the addition of magnesium is made to an alloy consisting entirely of the Al phase, the decomposition takes place extremely slowly. That small additions to the composition of an Al-Zn die-casting alloy may reduce growth caused by ageing is of immediate interest to those who use these alloys.

The use of ferrous and non-ferrous alloys at high temperatures is a most important problem. The ideal alloy should not soften to any appreciable extent at the maximum temperature at which it is likely to be exposed. It has, however, already been seen that alloys which age harden respond to different temperatures of heat treatment according to their compositions, but it is not always convenient or desirable to use an alloy which appears entirely suitable for the purpose in question; hence the need for the development of new alloys for specific purposes.

The question of creep at high temperatures plays a most important part in connection with this problem. The relation of ageing to creep is one of immense theoretical and practical importance. Cold work, *i.e.*, plastic deformation at room temperature, has a marked influence on the rate of age hardening; plastic deformation, such as occurs as a result of creep at elevated temperatures, must therefore have a far-reaching effect since the process of ageing is accelerated both by rise in the temperature of heat treatment as well as by the stress imposed. Creep is a subject which is, however, receiving much attention both from the experimental as well as the practical point of view.

The corrosion resistance of alloys which can be age hardened is another problem of industrial importance. The fact that the corrosion resistance of an alloy is least when the ageing process has not gone beyond the first stage is of practical importance. For a given composition of the alloy the desired mechanical properties are intimately connected with high corrosion resistance. The data regarding the ageing of alloys at different temperatures—if correctly used—will enable the manufacturer to produce alloys having the highest possible corrosion resistance associated with the best mechanical properties possible.

Another example of the practical importance of age hardening is seen in the similarity between the mechanism of the nitride hardening of steels and that of age hardening. Two theories of nitride hardening have been suggested: (i) that the presence of Al causes the precipitation of AlN during nitriding and that this finely dispersed phase is the cause of hardening; (ii) the substitution of Al atoms for certain of the Fe atoms in the several Fe-Ni phases in the same manner that the substitutional Fe-Al solid solution is formed. The marked increase in hardness is attributed to the severe lattice distortion accompanying this replacement.

Norton[58] has carried out an X-ray examination from which he concludes that although no diffraction lines corresponding to AlN appeared in the photograms, probably owing to its fine state of subdivision, the indirect evidence of its presence seems conclusive. He concludes therefore that the hardening of nitrided steels is due to the precipitation of AlN from solid solution.

These few examples illustrate the great importance of the phenomenon of ageing to industry. There are many other examples of its application, and it is probable that more will arise in the future. In certain cases ageing in an alloy may be a distinct hindrance, particularly when it may result in adverse changes occurring during creep at high temperatures. On the other hand, the development of high temperature alloy, may lie in the direction of producing alloys whose satisfactory properties cannot be attributed to age hardening, and it is probable that these latter alloys will be very complex, possessing little, if any, variation in solid solubility at different temperatures.

VI.—FURTHER INVESTIGATIONS.

From this brief digest on the phenomenon of ageing one or two problems stand out as being of vital interest. These are the effect of (*a*) grain boundaries, (*b*) diffusion, (*c*) cold work. Comparatively speaking, little is known about any of them from the purely scientific point of view and still less about their relationship to ageing; they are, however, of direct importance, since they have a very marked influence on the problem of age hardening. It is striking that when grain refinement of an alloy, which normally age hardens, is caused by the addition of an element which results in the formation of an insoluble phase (Fe on Cu-Al and Be-Cu alloys) the temperature at which age hardening first appears is raised. Is this a grain boundary effect or is there some other factor at work as yet undetected?

Again, the changes taking place within the lattice

during the first stage of age hardening is a very extensive problem, since it has yet to be shown whether or not the mechanism is the same for all alloy systems; each alloy will have its own peculiar problem which will become more complicated as the number of constituents is increased.

Finally, plastic deformation accelerates age hardening and, furthermore, there is some evidence that age hardening at room temperature may be related to strains set up as a result of severe quenching. If the latter is correct then the problem of ageing at room temperature is identical with that of accelerated ageing as a result of cold work. Hence, additional knowledge regarding the changes taking place in the atomic structure when deformation occurs may help also to solve the problem of ageing that takes place at room temperature in alloys of the duralumin type.

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Niobium-Iron and Niobium-Iron-Carbon Alloys.

NIOBIUM-IRON.

IT is fortunate that data for the correction of the conclusions drawn from the inadequate study of the niobium-iron system by R. Vogel and R. Ergang[1] were at hand in the paper published at about the same time by H. Eggers and W. Peter.[2] These investigators prepared their alloys by melting carbonyl iron and sheet niobium, containing 99·9 per cent. of the metal, in alumina crucibles. Those containing less than 10 per cent. of niobium were melted in a high-frequency furnace *in vacuo* (0·01 mm. of mercury), and those of higher niobium content in a Tammann furnace in an atmosphere of argon. Weights of about 40 or 50 grammes of each alloy were made in the form of cylindrical specimens, which were bored for insertion of thermo-couples, the borings serving for chemical analysis. As a preliminary, the alloys were annealed in stages. They were first held at about 50 deg. below the solidus, then at 50 deg. below each of the further transformations in the solid state with intermediate slow cooling. Thus, for example, the specimen was held for three hours at 1300–1400 deg., five or six hours at 1100–1200 deg., and twelve to twenty hours at 800–900 deg. Cent. The specimens were then subjected to thermal analysis and microscopical examination. The thermal analysis was carried out by taking time/temperature or temperature/temperature-difference curves. The phases stable at high temperatures were studied microscopically by quenching the specimen from these temperatures, with vigorous stirring, in water or in 10 per cent. caustic soda solution. Picric acid with the addition of 1 or 2 per cent. of nitric acid was used as etching reagent.

The niobium-iron diagram deduced by Eggers and Peter is shown in Fig. 1. It differs widely from that

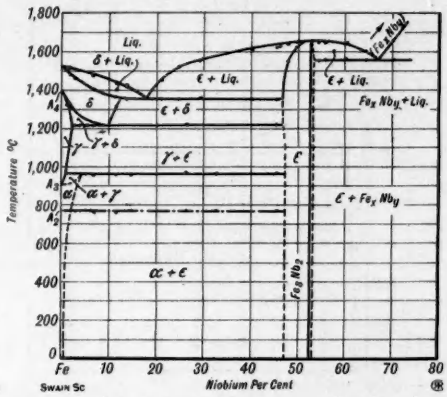
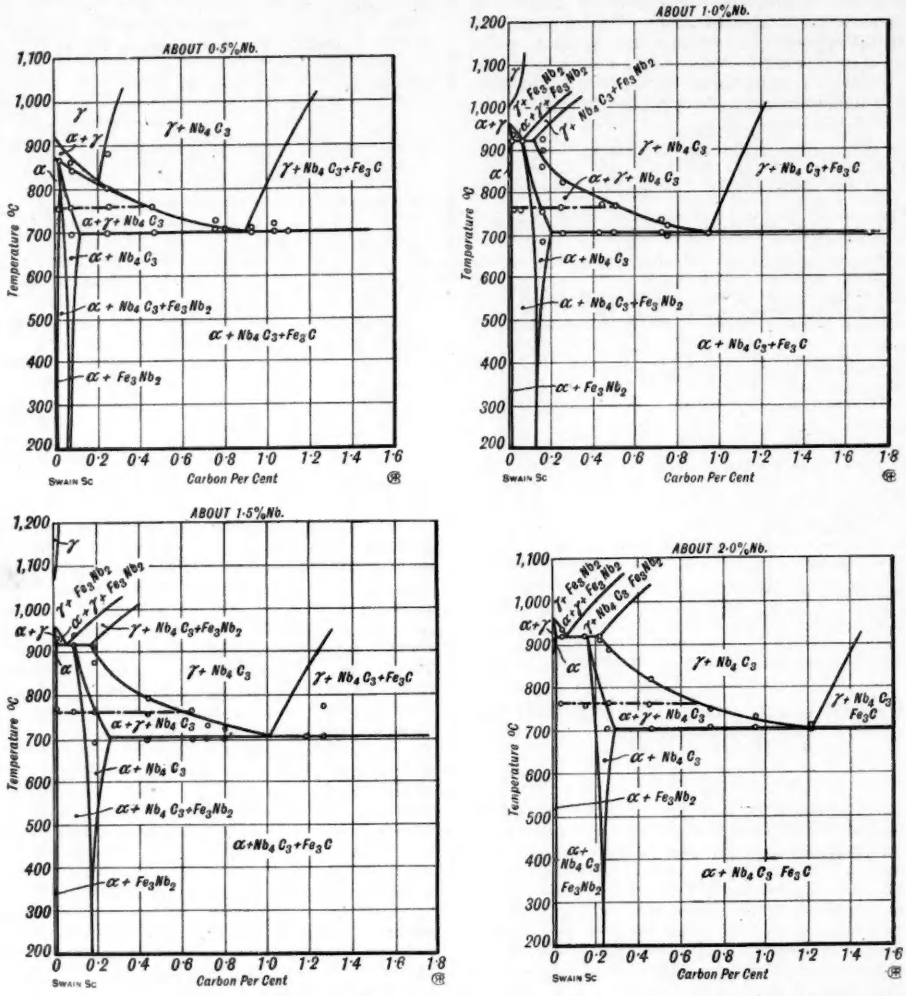


FIG. 1—*The Niobium-iron Diagram (Eggers and Peter).*

proposed by Vogel and Ergang. On the other hand, it bears a close resemblance to the tantalum-iron diagram by R. Genders and R. Harrison.[3] Iron was found to form an intermetallic compound with niobium, probably having the formula Fe_3Nb_2 and melting at 1650–1660 deg. Cent. This compound, the ε phase, forms with δ iron a eutectic containing 17·5–18 per cent. of niobium and melting at 1356 deg. Cent. On the niobium-rich side of Fe_3Nb_2 the ε phase forms a eutectic with another compound, Fe_xNb_y, of which the composition has not been determined. This eutectic contains 67–67·5 per cent. of niobium, and melts at 1560 deg. Cent. On cooling, the δ iron solid solution decomposes at 1220 deg. Cent. into a eutectoid of γ and ε. The γ iron transforms at 965 deg. Cent. into α iron containing about 5 per cent. of niobium and ε. Thus the γ field is contracted, but does not form a closed loop with a continuous α region up to the solidus temperature as found, for example, in the iron-vanadium and iron-molybdenum systems. The falling solubility of niobium in α iron provides for the temper-hardening phenomena observed by Vogel and Ergang.

Some interesting points are brought out by a comparison of the influence of niobium on iron with that of its close neighbours in the periodic system. The metals of the fifth group—vanadium, niobium, and tantalum—all possess the power of contracting the γ region. The solubility of the added metal in γ iron decreases with increasing atomic radius, but the influence of atomic radius is specially evident in the body centred cubic α or δ solid solutions. Vanadium and α iron form a continuous series of solid solutions at high temperatures, *i.e.*, above 1200 deg. Cent. Niobium at 1356 deg. is soluble in δ iron up to 12 per

cent. (7 atoms per cent.) and tantalum at 1430 deg. up to 7 per cent. (2·3 atoms per cent.). The metals of this group form with iron intermetallic compounds the melting point of which rises with increase in atomic number. In parallel with this rise there is a difference in the composition of the compounds (FeV, Fe_3Nb_2, and Fe_2Ta). The neighbours of niobium in the same series, zirconium and molybdenum, also show similar regularities. The γ region is constricted, and the solubility of the added metal in both α and γ iron is increased with increase in atomic number. The metals zirconium, niobium and molybdenum all form compounds of similar formulæ, viz., Fe_3Zr_2, Fe_3Nb_2, and Fe_3Mo_2.



FIGS. 2 TO 5—*Sections Through the Niobium-iron-carbon Diagram Parallel to the Iron-carbon Side (Eggers and Peter).*

NIOBIUM-CARBON.

The investigations of H. Eggers and W. Peter have been extended to cover the iron corner of the iron-niobium-carbon diagram at temperatures below 1050 deg. Cent.[4] This involves some knowledge of the niobium-carbon system, and of the composition of niobium carbides. C. Agte and H. Alterthum[5] found that a carbide NbC was formed by the reduction of niobium oxide by means of carbon at 1200 deg. Cent. Attempts to separate the carbide occurring in niobium steels were made on the following lines. Finely crushed 60 per cent. ferroniobium and wood charcoal were mixed in the ratio 5 : 1 and heated in a graphite pot in an atmosphere of argon. Incipient fusion occurred at 1600–1700 deg. Cent. Maintaining the temperature caused the heated mass slowly to toughen and become strong; then, raising the temperature to 2000 deg. Cent. did not again cause melting, and after two or three hours' heating a reaction product was obtained which was grey and brittle at atmospheric temperature. This mass was pulverised and subjected for twenty hours to the action of 10 per cent. hydrochloric acid. The undissolved residue was

filtered with the exclusion of air and was found to contain carbon 4·04, niobium 71, iron 25 per cent. At the same time, an X-ray analysis showed that the mixture contained Fe_3Nb_2. If all the iron is assumed to be combined with niobium to form Fe_3Nb_2, the atomic proportion of the remaining niobium to carbon is 4·08 : 3, *i.e.*, Nb_4C_3. The carbide residue was extracted in a similar way from an alloy containing 9 per cent. of niobium and 3 per cent. of carbon. It was free from iron, showing that no double carbide of iron and niobium occurs. Analysis gave carbon 10·5, niobium 89·5 per cent., corresponding to the atomic proportion of niobium to carbon of 4 : 3·6. Although this might be taken with equal justification to represent NbC or Nb_4C_3, X-ray examination of the residue showed that it contained the same carbide as was present in the residue from the alloy of higher niobium content. It was therefore concluded that the only niobium carbide present in niobium steels was Nb_4C_3. The formula is thus of the same type as that for vanadium carbide, V_4C_3.

Niobium-iron-carbon.

The ternary alloys were prepared from Armco iron, commercially pure niobium and Swedish white iron. There were five series of alloys containing approximately 0·2, 0·5, 1·0, 1·5, and 2·0 per cent. of niobium. In each series the carbon varied from less than 0·04 upwards, reaching 1·2 per cent. with 2·0 per cent. of niobium and 2·4 per cent. with 0·2 per cent. of niobium. The low-niobium alloys were made in a high-frequency furnace. Others were made in a special carbon-spiral vacuum furnace under a pressure of 0·2 mm. to 0·3 mm. of mercury at 1800 deg. Cent.

The phases which appear in the iron corner of the niobium-iron-carbon diagram are the α and γ solid solutions, iron niobide Fe_3Nb_2, cementite Fe_3C, and niobium carbide Nb_4C_3. With the exception of the γ solid solution all these phases are stable at atmospheric temperature. Sections across the ternary diagram at 0·5, 1·0, 1·5, and 2·0 per cent. of niobium are shown in Figs. 2 to 5. These are based on the results of thermal analysis and microscopic examination of slowly cooled or quenched specimens, etched in all cases with picric acid containing 1 or 2 per cent. of nitric acid. Features of the diagrams are the two four-phase planes, one at 920 deg. and the other at 705 deg. Cent. At 705 deg. the γ phase decomposes according to transformation

$$\gamma \rightleftarrows \alpha + Fe_3C + Nb_4C_3.$$

At 920 deg. a non-variant transposition takes place according to the equation

$$\gamma + Fe_3Nb_2 \rightleftarrows \alpha + Nb_4C_3.$$

The magnetic change at about 760 deg. Cent. was observed in all the steels containing the α solid solution at that temperature. The three-phase region $\alpha+\gamma+Fe_3C$ must have been very narrow in the ternary alloys, as it had already disappeared before 0·2 per cent. of niobium was reached. The γ region is rapidly reduced in size as niobium increases, with a corresponding enlargement of the $\gamma+Nb_4C_3$ region. The carbon content at which free Fe_3C appears above the eutectoid temperature 705 deg. Cent. is raised from 0·9 to 1·2 per cent. as the niobium rises to 2 per cent. The boundary of the $\alpha+Nb_4C_3$ and $\alpha+Nb_4C_3+Fe_3C$ regions at atmospheric temperature occurs at the following positions :—

With Nb, per cent....	0·2	0·5	1·0	1·5	2·0
With C, per cent. ...	0·04	0·07	0·13	0·18	0·21

These limits are referred to as the lowest carbon contents at which pearlite can appear in the structure. Since, however, pearlite is formed at the eutectoid temperature the carbon contents chosen should more accurately be the upper limits of the $\alpha+Nb_4C_3$ fields at that temperature. These are a little, perhaps 0·04 to 0·07 per cent., higher than the figures given above. The $\alpha+Nb_4C_3$ region is of some interest. Though broad at about 700 deg. Cent., it narrows down with falling temperature to the figures mentioned above, since the α solid solution precipitates either Fe_3C or Fe_3Nb_2 according as the carbon content is higher or lower than the above limits. Expressed in another way, the niobium combines with the carbon present, and if there is an excess of either of these elements it combines with iron, an excess of niobium forming Fe_3Nb_2 and an excess of carbon forming Fe_3C.

These papers by Eggers and Peter form a substantial contribution to our knowledge of the niobium-iron-carbon equilibrium and should be of considerable assistance in explaining the action of niobium in the various uses to which it is now being put in the steel industry.

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Tin-Plate Manufacture in Germany.

Contemporary practice in the tin-plate industry in Germany has been reviewed by Fritz Peter in a report to the Materials Committee of the Verein deutscher Eisenhüttenleute.* The author states that, as tin is a relatively expensive metal, coatings must be as thin as possible consistent with their affording sufficient protection to the underlying steel. A thickness corresponding to 25 grammes of tin per square metre should suffice, but in actual practice nearer 35–50 grammes per square metre is commonly found, and even more than this in certain cases. The necessary amount of tin coating is considered to be governed to a certain degree by the properties of the basis metal, which should therefore have a smooth, chemically clean surface. The important point is made that variations in properties of the steel basis sheets result in the necessity of exceeding a thickness of coating which would otherwise be satisfactory from both technical and economic viewpoints. Cold reduction of from 1 to 2½ per cent. did not appear to have the influence on the tinning properties which has usually been ascribed to it. W. Kramer has stated previously that 5 per cent. cold reduction (the lower critical limit of cold deformation which should therefore not be exceeded if subsequent annealing is to be avoided) resulted in definite improvement from the tinning standpoint, owing to its effect in removing roll marks and scale pits.

Normalising is carried out in many tin-plate works and results in more uniform mechanical properties of the steel. The process is, however, not universally approved by tinners, and this is apparently partially attributed to the fact that normalised sheets, on account of their having been in contact with burning gases in the furnace chamber, are not so well cleaned in pickling as box-annealed sheets which have been exposed to the reducing action of hydrogen and

* *Stahl und Eisen*, 1938, 7, 165.

carbon monoxide. It is also noticed that if normalised sheets are pickled, washed, and dried they rust more easily than box-annealed sheets.

Normalised sheets are usually pickled, polished (cold rolled), and then softened by a temper anneal. The final white pickling before tinning should be as light as possible and preferably carried out with an acid concentration of from 3 to 7 per cent. The temperature should not be higher than 50 deg. Cent. with a hydrochloric acid pickle and not above 85 deg. Cent. if sulphuric acid is used. This last operation should be regarded only as a light final clean-up before tinning, otherwise the surface finish suffers. The tinning of sheets immediately after pickling is not recommended, since tests have shown that if the sheets are kept in slightly acidified water for some hours the hydrogen absorbed during pickling is evolved and the tin coating is consequently less porous.

TINNING MACHINES.

Improvements have continued to be made in the design of tinning sets, although recent developments cannot be considered to be revolutionary. Tinning sets are usually of one of two types: the "Abercarn," which is a double sweep pot, and the "Aetna," which is single sweep. The "Abercarn" type of machine has two separate compartments permitting independent regulation of the temperature of the molten tin at the flux and exit ends. Such machines may be made to carry two or three sheets side by side simultaneously, and are usually fed by hand; the speed of travel is regulated so that the total passage takes about twelve seconds. The "Aetna" type of machine is single sweep, only a small bridge dividing the entry and exit ends of the pot. This is a higher speed machine, the total time of travel being about four seconds. The machines may carry either three or four pairs of rollers in the grease pot.

There is little difference between tin-plates produced in these two types of tinning machine, although the slower running "Abercarn" type is said to yield a somewhat brighter plate. Characteristic needle-like markings appear on tin-plates tinned in the "Aetna" type machine and are considered to be due to vibration of the surface of the palm oil and the rapid draining of the oil from the still molten coating. Under standard conditions the "Abercarn" machine usually gives somewhat thinner coatings, as the sheets remain longer in the vertical position while the tin is still molten. Both machines, however, give very satisfactory coatings. The single-sweep type machine is smaller and it may be preferred in cases where saving of space is an important factor. There are, of course, numerous machines intermediate between these two types. The asbestos grease pot brushes are adjusted according to the speed of tinning and besides regulating the thickness of the coating they also exert a cleaning action on the rollers. Stop plates are used between the brushes and the nips to prevent the flowing of tin underneath the rollers. The rollers themselves should have a clean surface and be accurately turned. It is important also that the mechanical arrangements should be such that they are driven uniformly and smoothly, maintaining a true surface during long periods of use. The promotion of a smoother drive has been the subject of many experiments, such as the use of ball or roller bearings and the provision of a special gear drive to the top pair. Another patent refers to the use of a special arrangement of grease pot brushes resulting n economies in tin yield. The most satisfactory method of heating the tin appears to be by electric immersion heaters.

TINNING.

Zinc chloride is employed almost exclusively as a flux, although certain additions may be made, *e.g.*, stannous chloride, aluminium chloride, potassium fluoride, sal ammoniac, &c. The usual addition made is one of ammonium chloride and it may be encountered in many proprietary fluxes. Although additions of from 5 to 25 per cent. of ammonium chloride have been recommended from time to time, in the author's experience the percentage should be kept below 8 per cent., since a greater concentration than this causes increased porosity of the tin coating. The addition of tin chloride is in any case superfluous, because this is formed during the fluxing operation. It is important that satisfactory operating conditions should be maintained by frequent additions of small quantities of fresh flux, and the regular removal of dross and scum. The removal of impurities is preferably carried out by means of a perforated ladle at two-hour intervals. The life of a flux depends on the amount of work it has to do (that is, the amount of impurities to be fluxed away from the surface of the steel), on the rate at which it picks up tin and iron from the bath and sheets, and on the rate of formation of zinc hydroxide by reaction with the water taken in on the sheets. On the average 50 to 60 grammes of zinc chloride are utilised for every basis box of tin-plate (*i.e.*, from 20·2 to 22·6 grammes per square metre), and it has not been found possible to effect any significant savings on this flux yield. Attention should be paid to the way in which the sheets are introduced into the flux and to the amount of water that they carry, irregularities at this stage resulting in flux being carried forward in the tin pot even as far as the palm oil. Such conditions give rise to increased porosity, streaks, and a generally unsatisfactory appearance.

No alloying elements are permissible in a tin bath and the metal should be as pure as possible. Lead, however, is nearly always present and up to 0·1 per cent. of lead has been encountered, though more usually the concentration of this element will be from 0·03 to 0·05 per cent. Molten tin is also capable of dissolving up to 0·3 per cent. of iron at 300 deg. Cent., this metal coming both from the black plates and from the metal of the tin pot itself. Attack on the metal of the tin pot is particularly severe at the flux-air and oil-air interfaces. Local overheating is a contributory cause of increased uptake of metal from the tin pot.

Copper may be introduced into the tin bath if copper-bearing steel sheets are being put through. Also in certain cases the presence of copper in the tin bath has been traced to the use of bronze pickling equipment. The effect of such small concentrations of copper (up to 0·2 per cent.) is to cause spangling of the tin coating, but they are not otherwise deleterious.

The temperature of the tin is maintained at about 300 deg. Cent. at the flux end and 240 deg. Cent. at the exit end. The thickness of the tin coating, besides depending on the temperature of tinning, depends also on the setting of the tinning rolls and of their brushes. The length of time of tinning is, on the other hand, considered to be almost without effect on the coating thickness owing to the rapid formation of an intermediate layer of $FeSn_2$, which prevents continued reaction. The palm oil in the compartment at the exit end, which is maintained at a temperature only

a few degrees above the melting point of tin, serves the double purpose of keeping the tin in molten condition while the thickness of coating is regulated by the grease pot rollers, and of protecting the coating from oxidation. The palm oil has an acid reaction and after some time forms tin soaps. Efforts to find a suitable substitute for palm oil have so far been unsuccessful, either for technical or economic reasons. Such a material would have to have low viscosity, to be non-oxidising, odourless and tasteless, and to have a melting point less than 130 deg. Cent. and a flash-point of over 320 deg. Cent.

The coating must be solid before it is gripped by the manipulating rollers at the top of the grease pot, and if difficulty is encountered it may be cooled above the top of the grease pot by an air blast. This device may be used especially when the tinning speed is high. The consumption of palm oil is about 150 grammes per basis box of sheets tinned.

Utilisation of Residues.

According to recent estimations, used flux may contain up to 10 per cent. of tin, but it is frequently contaminated with palm oil, which makes it extremely difficult to work up. Free tin is separated by washing away the flux. The hard tin ($FeSn_2$), being heavier than the unalloyed metal, collects at the bottom of the tin pot and is removed every week. Dross is usually considerably contaminated with palm oil, from which it is freed by saponification of the latter with caustic soda. The separated residue is then melted to yield a product containing 50 to 60 per cent. of tin, which is sent to refineries, along with the other residues mentioned above, for recovery of tin.

Cleaning.

The medium for cleaning tin-plates employed to-day is usually bran, the earlier mixtures of sawdust and gypsum having been found somewhat less efficient. A recent type of branning machine is illustrated in the original article. It is emphasised by the author that the correct setting of the rollers and control of the supply of absorbent material is necessary for the production of sheets with a clean brilliant surface. Although the tin coating is relatively soft the fabric cleaning rollers of the machines may in certain cases be partially replaced by steel rollers. The use of bran is also to be recommended, since the oil impregnated material may be sold for use as a concentrated feed.

If wet cleaning methods are used, the palm oil is not recoverable in this way, and it is also considered that the appearance of the tinplates is not quite so brilliant after wet cleaning. The costs of cleaning form at present only a small percentage of the total cost of production and endeavours to economise would not therefore result in very great advantages. It is considered, however, that economies would result from standardisation of the size of sheets and by packing the sheets in larger units (increasing the weight of a basis box by 50 per cent.).

Fissures in Railroad Rails.

The Fourth Progress Report of the Joint Investigation of Fissures in Railroad Rails, by Herbert F. Moore,* opens with a brief review of the work previously carried out, and recalls the evidence which has been offered to show that internal fissures in rails start from minute shatter cracks in the rails as rolled, which spread under occasional heavy wheel loads to which the rail may be subjected in service. It is further stated that studies of the controlled cooling process indicate that it is highly efficient in eliminating shatter cracks.

Fresh work of the Committee is dealt with under the following headings :—

II. Temperature Limits for Controlled-cooling of Rails.

A series of experiments were carried out at the Ensley mill of the Tennessee Coal, Iron and Railroad Company, in which 2ft. lengths of rail from a series of heats coming from the mill were cooled in four ways, as follows :—

(1) Cooled in air on the mill floor to serve as "control" specimens.

(2) Placed in cooling boxes at 900 deg. Fah. (482 deg. Cent.) and removed at intervals of 100 deg. Fah. (55·5 deg. Cent.).

(3) Placed in cooling boxes at 900 deg. Fah. (482 deg. Cent.) and removed after approximately twenty-one hours, the rate of cooling being varied by the amount of insulation used.

(4) Placed in cooling boxes at 100 deg. Fah. (55·5 deg. Cent.) intervals from 900 deg. Fah. (482 deg. Cent.) to 200 deg. Fah. (93·5 deg. Cent.), and removed after twenty-one hours.

Etch tests were made on longitudinal slices from all specimens and from the results obtained from those heats which showed shatter cracks in the air-cooled specimens (1), the following conclusions were drawn :

(1) Rail specimens cooled in air to temperatures above 300 deg. Fah. (148 deg. Cent.) before being placed in boxes developed no shatter cracks.

(2) Rail specimens placed in boxes after specimens had cooled to 200 deg. Fah. (93·50 deg. Cent.) did develop shatter cracks; evidence that the cracks formed between 300 deg. Fah. (148 deg. Cent.) and 200 deg. Fah. (93·50 deg. Cent.).

(3) Rail specimens placed in boxes at 900 deg. Fah. (482 deg. Cent.) and removed at 600 deg. Fah. (316 deg. Cent.) or lower showed no shatter cracks, while specimens out at 800 deg. Fah. (426 deg. Cent.) and 700 deg. Fah. (371 deg. Cent.) developed shatter cracks. This seems to indicate that while shatter cracks actually did not form above 300 deg. Fah. (148 deg. Cent.), nevertheless, slow cooling above that temperature was effective in inhibiting their formation below that temperature.

(4) In all tests shatter cracks were developed only in rail specimens which cooled from 900 deg. Fah. (482 deg. Cent.) to 200 deg. Fah. (93·5 deg. Cent.) in less than four hours.

(5) Placing the rails in controlled-cooling boxes at temperatures of 900 deg. Fah. (482 deg. Cent.) or below did not lower the Brinell hardness of the rails. This is in agreement with test results on seventy-five pairs of controlled-cooled and air-cooled rails previously tested.

While these tests indicated that the present practice in most mills of keeping rails in control cooling boxes from twenty-four to thirty-six hours might be somewhat modified, yet it is emphasised that none of the heats tested contained so many shatter cracks as the worst heats previously examined, and that therefore it cannot be concluded that these results would apply to all heats of rail steel.

A second series of tests has recently been completed at the mill of the Dominion Steel and Coal Corpora-

* University of Illinois Bulletin, July 19th, 1938. For Third Report see The Metallurgist, Dec. 31st, 1937, p. 92.

tion, Ltd., at Sydney, Nova Scotia, but the results are not yet compiled.

III. METALLOGRAPHIC AND HARDNESS TESTS OF END HARDENED RAILS.

IV. MECHANICAL TESTS OF SPECIMENS FROM END HARDENED RAILS.

V. EFFECT OF HARDNESS ON TENSILE AND IMPACT PROPERTIES OF RAIL STEEL.

VI. ROLLING LOAD TESTS FOR BATTER OF RAILS.

The investigations under these sections have afforded some very interesting results, but it is somewhat difficult to see what direct relation they bear to the study of internal fissures in rails.

Numerous methods of end hardening, both at the mill and in the track, are briefly described, and numerous tests of rails end hardened by these processes have been made to determine (*a*) the depth and hardness of the treated zone; (*b*) the relative mechanical properties of the hardened and unhardened metal; and (*c*) the effect of end hardening on batter as produced in the rolling load machine.

As regards (*a*) the results obtained from different processes vary from producing a hardened zone extending throughout the rail head for a distance of some 3in. to 9in. from the end; to a shallow surface hardening extending only about 1in. from the end. The increase in hardness varies from about 6 to 17 points on the Rockwell C scale. Mechanical tests show generally an increase in both strength and toughness in the hardened zone.

The batter tests show some rather remarkable results. Rail ends hardened to between 35 and 40 Rockwell C all show the minimum amount of batter after 1,000,000 cycles (0·005in. to 0·006in.) with very considerable improvement over the same rails unhardened, in which the batter varies from 0·015in. to 0·034in. Rail ends hardened to a lesser degree (28–32 Rockwell C), however, show in the three examples tested, in one case no improvement (the batter for both hardened and unhardened being 0·010in.), in another a slight improvement (0·034in. to 0·0275in.), and in the third an actual increase in batter (0·024in. to 0·0245in.) in spite of an increase of hardness of from 28 to 32. The variation in the results of batter tests in the unhardened rail ends, which gave an amount of batter after 1,000,000 cycles of from 0·010in. to 0·034in., the extremes having practically the same hardness (28), is difficult to understand, and it is a pity that further details of these rails, including their chemical composition, are not given. It is suggested that surface decarburisation may be one factor.

In Section V some experiments are described in which specimens of rail steel quenched and tempered to various degrees of hardness were subjected to tensile and unnotched Charpy impact tests. The results indicate a maximum toughness at about 40 Rockwell C hardness with a very decided drop above 50 Rockwell.

VII. NON-DESTRUCTIVE TESTS.

A brief description is given of methods evolved to measure the damping factor of rails vibrated at their natural frequency with a view to obtaining a non-destructive test for shatter. Tests with the final scheme are now in progress, but from the earlier experiments it is anticipated that positive results may be obtained.

VIII. MISCELLANEOUS TEST RESULTS.

Detector cars have been run over a number of test locations, but in only one location have internal fissures been found, and these were all in rails from two heats, both of which were known to have contained shatter cracks. It is not stated whether any or all of the rails in the other locations, where no fissures have developed, had been control cooled or normalised.

Other tests in this section deal with some investigations on web failures and the effect of cracks in reducing endurance limits of rail steel.

The report concludes with three appendices dealing (*a*) with Formulæ and Diagrams for Computing Shearing Stresses in Rail Head which are Due to Direct Action of Wheel Load; (*b*) The Effect on Wheel Loads of Irregularities of Wheels and Track and (*c*) Notes on the Relation of Rockwell C Hardness to Brinell Hardness Numbers.

No further investigations are reported (in continuation of Section VI of the third report) on the influence of hydrogen on the susceptibility of rail steel to the formation of shatter cracks. There is now considerable evidence available to show that hydrogen is a very important factor, but much more experimental work is required to elucidate both possible sources of its introduction into steel during manufacture, and also its action in giving rise to shatter cracks. Work on these lines should be of very great value.

Finally, it is thought that some reference might be made to the fact that the process of controlled cooling of rails is now almost universal in all American rail mills. As clearly emphasised in these reports, this process is an efficient means of preventing shatter, and thus as controlled cooled rails replace older rails which were cooled out on the hot bed, the serious and dangerous problem of the transverse fissure should be a gradually diminishing one.

Iron-Titanium-Carbon Alloys.

THE constitution of the iron-titanium-carbon alloys is imperfectly known. In a study of some titanium steels, K. Tamaru[1] concluded that the iron-carbon eutectic (carbon 4·3 per cent. at 1135 deg. Cent.) was moved to a lower carbon content and higher temperature, and that the carbon limit of the γ region was reduced. In addition, the carbide-forming property of titanium was well recognised and has been widely applied. A substantial contribution has now been made to the subject by W. Tofaute and A. Büttinghaus[2] in a paper on "The Iron Corner of the Iron-Titanium-Carbon System." The materials employed were sintered carbonyl iron, wood charcoal for carburising the melts, and pure titanium prepared by thermal dissociation, and obtained from the Deutsche Gold- und Silberscheideanstalt. Melts of 2 kilos. to 5 kilos. were made in a basic high-frequency furnace, and after fusion of the carbonyl iron titanium was added without any previous reduction by aluminium or silicon. The titanium losses were high on account of oxide and nitride formation, and it was found that the viscous character of the melt increased so markedly with increasing titanium content that it was scarcely possible, even with strong overheating, to cast the iron alloy with 10 per cent. of titanium. The steels with high titanium and carbon content were also extraordinarily viscous on account of the large amount of titanium carbide present.

In forging trials, from an initial temperature of 1000 deg. to 1050 deg. Cent., the carbon-free iron-titanium alloys proved to be readily forgeable with titanium contents up to 6 per cent. Forging of the

iron-titanium-carbon alloys was also possible with higher titanium contents, a limit being reached with 0·3 per cent. carbon and about 9 per cent. titanium. The alloys were annealed for twenty hours at 1000 deg. Cent., and slowly cooled to room temperature. This treatment proved to be adequate, as equilibrium was relatively easily attained. Among the tests applied were microscopical and X-ray studies of structure, and determinations of hardness, electrical conductivity, magnetic, and dilatometric behaviour, more complete details of which are published elsewhere.[3]

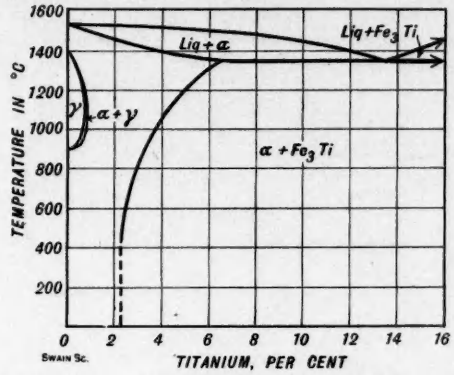


FIG. 1—*Part of the Iron-Titanium Diagram (Tofaute and Büttinghaus).*

THE BINARY SYSTEM FE-TI.

The limits of the γ field were determined by thermal analysis and dilatometry and the temperature of the eutectic change was redetermined. This was found to be 1350 deg. Cent. in contrast to 1298 deg. Cent. shown in the diagram of J. Lamort.[4]

The limit of solubility of titanium in iron at the eutectic temperature was found to be 6·3 per cent. the diagram up to about 7 per cent. of titanium appears to be satisfactorily indicated by this work, but the constitution of the alloys with a higher range of titanium content is still in doubt. The nature of the phase which separates from the α solution is open to question. H. Witte and H. J. Walbaum[6] in a "Thermal and X-ray Investigation of the Iron-Titanium System," were unable to identify the compound Fe_3Ti of Lamort's diagram, although its existence had been confirmed by W. Jellinghaus,[7] who found its crystal structure

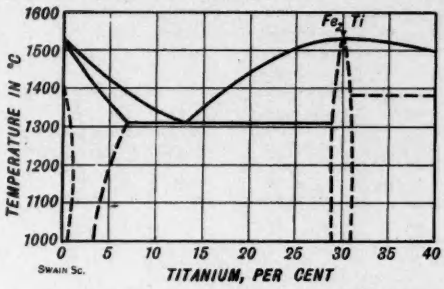
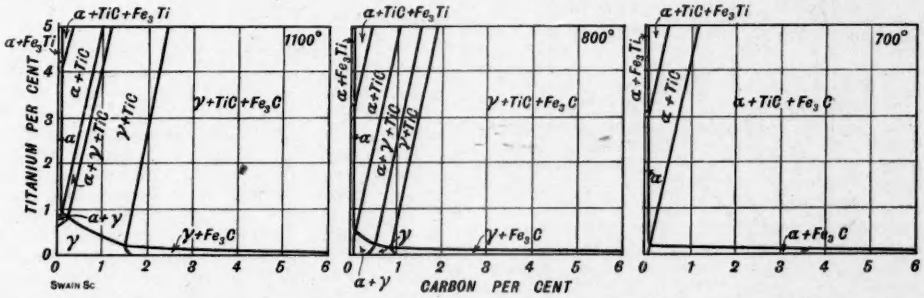


FIG. 2—*Part of the Iron-Titanium Diagram (Witte and Wallbaum).*

to be similar to that of Al_3Ti. On the other hand, they found a compound Fe_2Ti having the same crystal structure as Zn_2Mg, a density of 6·75 g. per c.c., and a melting point of 1530 deg. Cent. Clear microscopical evidence was obtained of eutectic in the alloys with 29 and 33 per cent. of titanium, on each side of the homogeneous alloy containing 30 per cent. of titanium (the composition corresponding to Fe_2Ti). Over the range 22 to 38 per cent., only the lines of Fe_2Ti were found in the Debye photograms. Below 22 per cent. iron lines appeared in the diagram and above 38 per cent. there were indications of a new



FIGS. 3 TO 5—*Sections at 1100 deg., 800 deg., and 700 deg. Cent. through the Iron Corner of the Iron-Titanium-Carbon Diagram.*

confirming Lamort's figure, but at room temperature it was no more than 2·5 per cent. The separation of Fe_3Ti from the α solution during cooling was investigated by a study of structure, hardness and magnetic properties in relation to tempering temperature and time of reheating. The revised diagram of the binary system is shown in Fig. 1.

Some further modifications of the solubility limits have been proposed by R. Vogel and R. Ergang,[5] who found the solubility of titanium in α-iron to be 6·9 per cent. at the eutectic temperature, falling to 2 per cent. at 700 deg. Cent. With this possible amendment the character of phase. The proposed constitutional diagram is shown in Fig. 2.

THE TERNARY SYSTEM FE-TI-C.

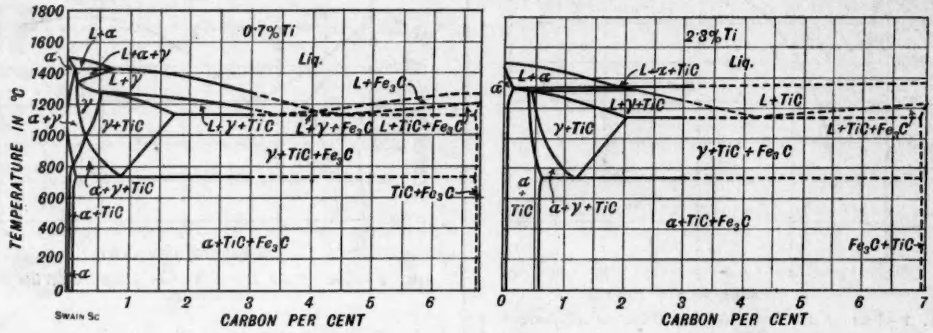
In the investigation of this system by Tofaute and Büttinghaus the iron-titanium compound was assumed on the evidence provided by Jellinghaus to be Fe_2Ti, and will therefore be referred to by this formula, though it will be understood that its chemical composition is at present doubtful. The constituents separating from the liquid alloys were found to be α solid solution, γ solid solution, Fe_2Ti, TiC, and Fe_3C. The approximate fields of primary crystallisa-

tion were ascertained for all these, except Fe_3C, as the alloys with primary Fe_3C have no practical importance.

In studying the subsequent changes thermal determinations were made of the transformations corresponding to the A_1 and A_3 points in carbon steels by the aid of the Saladin method and by thermal dilatation curves. These data were supplemented by hardness tests and by microscopical examination. The most satisfactory etching medium for the detection of titanium carbide in the presence of α and γ solutions was found to be the potassium ferricyanide reagent of T. Murakami and K. Someya.[8] Titanium carbide could be distinguished from iron carbide by etching with alkaline sodium picrate solution which stains iron carbide black, but does not attack titanium carbide. A copper reagent served to distinguish this compound from Fe_3Ti, the surface of which was much more readily coppered than that of TiC.

Carbide residues were separated from some of the alloys. An X-ray analysis of residues derived from alloys of different iron content gave a constant lattice parameter of 3·34 Å for the titanium carbide, indicating that there was no appreciable solubility of iron in titanium carbide.

Below the solidus the equilibrium relations were mainly governed by (i) the precipitation of titanium and iron carbides from the γ solid solution during cooling, and (ii) the γ–α transformation. The progressive restriction of the γ region with falling temperature is shown by Figs. 3 and 4, and its final disappearance below the transformation temperature by Fig. 5. The effect is more clearly shown in the sections at constant titanium content (Figs. 6 and 7). With 0·7 per cent. of titanium the γ region is still present, though much smaller. When the titanium content reaches 1·2 per cent. it is no longer present. The changing form of the γ field is illustrated better by Fig. 8 in which the sections for each titanium content are projected on to the iron-carbon plane. With increasing titanium the α field becomes more and more contracted until at 1 per cent. of titanium only a point remains. At the same time the α→γ transformation in the low carbon alloys is displaced to a higher temperature, until with 1·2 per cent. of titanium the alloys consist of α or α+TiC right up to the melting point. With higher titanium content these two regions widen still further, so that, with 2·3 per cent. of titanium and up to 0·4 per cent. of carbon, the alloys were entirely ferritic up to their melting points. Evidence was obtained of the separation of Fe_3Ti, as well as of TiC from the solid solution containing over 3 per cent. of titanium.



FIGS. 6 AND 7—*Sections through the Iron-Titanium-Carbon System at Different Titanium Contents.*

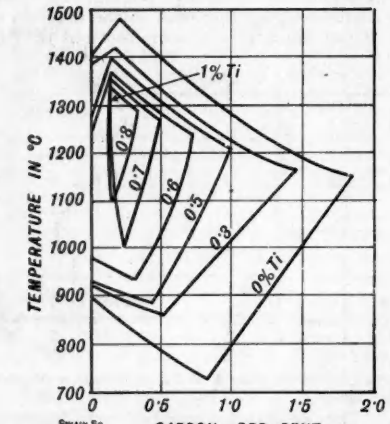


FIG. 8—*Projection on to the Plane of the Iron-Carbon System of the Limits of the γ Field in Alloys of Increasing Titanium Content*

The diagram reveals the limited field of technical utility of titanium steels. Titanium, like chromium, produces a restriction of the γ field, but the effect of 0·8 per cent. of titanium is as great as that of 15 per cent. of chromium. As the stable range of the homogeneous phase is very small, hardening of the steels is only possible within very narrow concentration limits. In the two and three-phase fields bounding the γ region the hardness of the alloys increases only gradually with increased hardening temperature. The quench-hardenability of steels containing titanium is thus greatly reduced. Titanium-rich low carbon steels are, in fact, not hardenable at all, and remain ferritic up to the melting point.

With very high titanium contents, for example, 4 to 22 per cent., hardening can be brought about by the precipitation of Fe_3Ti (or Fe_2Ti), but the metallurgical production of these alloys is difficult on account of the viscosity of the molten material.

PRACTICAL CONCLUSIONS.

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